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An Examination of the Relationship Between SERS Intensities and Surface Concentration for Pyridine Adsorbed at the Gold/Aqueous Solution Interface

by

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AN EXAMINATION OF THE RELATIONSHIP BETWEEN SERS  
INTENSITIES AND SURFACE CONCENTRATION FOR PYRIDINE  
ADSORBED AT THE GOLD/AQUEOUS SOLUTION INTERFACE

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Understanding the relationship between surface enhanced Raman scattering and surface concentrations of molecules is essential to gaining an understanding of the mechanism of SERS. At the metal/solution interface very few such studies have been reported [1,2]. This is primarily due to a lack of surface concentration data for the substrate/adsorbate systems most frequently studied in SERS - a consequence of the difficulty in determining this parameter for adsorbates on solid electrode surfaces. During the past few years we have demonstrated that reliable surface concentration data can be obtained for molecules adsorbed at the metal/solution interface using an electrochemical technique known as chronocoulometry [3,4]. Here we present SERS data for pyridine adsorbed at the polycrystalline gold/aqueous solution interface, for which we also have data for surface coverage. SERS data for both smooth and rough electrode surfaces are presented.

Shown in Fig. 1 is an example of a SERS spectrum of pyridine adsorbed onto a smooth polycrystalline gold electrode surface which was under an applied electrode potential of -0.4 V. Two bands can be seen in the spectral region shown. Variations in the integrated intensity of the  $1010\text{ cm}^{-1}$  band (from the totally symmetric ring breathing mode of pyridine) have been studied as a function of the bulk pyridine concentration and the degree of surface roughness.

The area under the  $1010\text{ cm}^{-1}$  band was measured for the various bulk pyridine concentrations and compared to the surface concentration data for the same bulk concentration. Shown in Fig. 2 is a plot of the normalized  $1010\text{ cm}^{-1}$  band area,  $I_N$ , as a function of the surface concentration,  $\Gamma$ , of pyridine for a bulk pyridine concentration of  $1 \times 10^{-3}\text{ M}$ . The data presented in this figure were obtained from a smooth gold electrode surface. The electrode potential changes, of course, as  $\Gamma$  changes. As Fig. 2 shows, the SERS data track the surface concentration data very well for values of  $\Gamma < 3.2 \times 10^{-10}\text{ mol cm}^{-2}$ . All such curves pass through the origin of the coordinate system. This indicates that the Raman signal arises from adsorbed pyridine molecules.

Normalized band area-surface concentration curves obtained for other pyridine concentrations ( $4 \times 10^{-5}\text{ M}$ ,  $10^{-4}\text{ M}$  and  $3 \times 10^{-3}\text{ M}$ ) were very similar to that which is presented in Fig. 2. In fact the position of the maximum occurred at the same value of the surface concentration (viz.  $4.0 \times 10^{-10}\text{ mol cm}^{-2}$ ), independent of the bulk pyridine concentration. This observation is

important from the point of view of the nature of the SERS mechanism which is operating in our system.

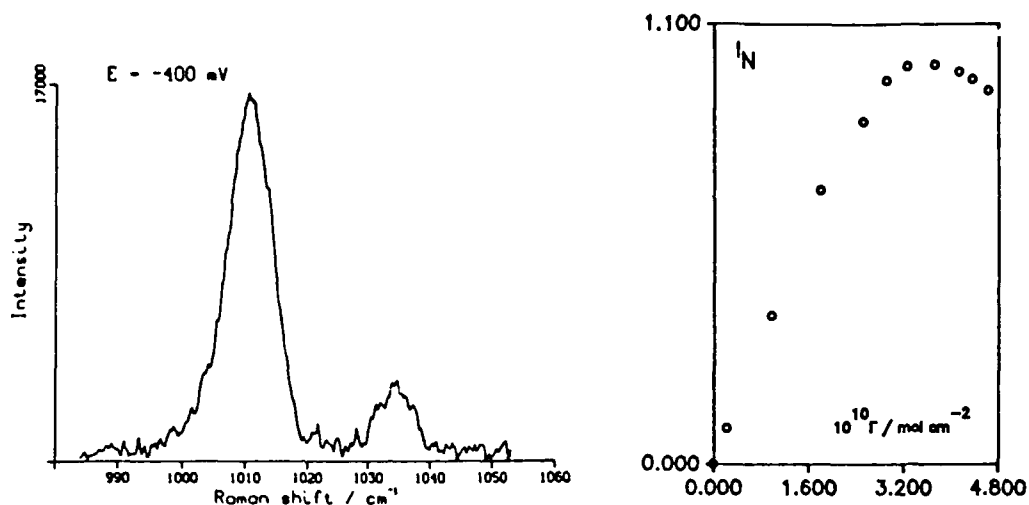


Fig. 1: SERS spectrum of pyridine adsorbed onto a smooth polycrystalline gold electrode surface from a solution containing  $3 \times 10^{-3}$  M pyridine, 0.1 M KClO<sub>4</sub>. Exciting line - 680.471 nm, laser power 150 mW, 90 accumulations, integration time 1 s.

Fig. 2: Plot of the normalized 1010 cm<sup>-1</sup> band area versus the surface concentration of pyridine for a bulk concentration of  $1 \times 10^{-3}$  M.

The SERS data for pyridine adsorbed on a roughened gold electrode surface do not correspond well to the surface concentration data. The SERS generates strong signals whereas the surface concentration data suggest that no signal should be observed. The quantitative nature of the band-area potential curve also depends on the degree of surface roughness.

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